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(54) SEMICONDUCTOR PHOTOCATALYST AND HYDROGEN PRODUCTION USING THE SAME

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a semiconductor photocatalyst which has high hydrogen generation efficiency by photodecomposition of water and is not photodecomposed at all and can use visible light and infrared light as well as ultraviolet light and can be continuously used.

SOLUTION: Semiconductor particles having $\leq 1 \mu\text{m}$ particle size of titanium oxide, cadmium sulfide or the like carrying 0.5 to 5 wt.% platinum are capsuled to ≤ 2 wt.% coating quantity by a polymer of a vinyl monomer such as acrylic ester, methacrylic ester, styrene, and vinyl acetate, or a polymer of polyvinyl potassium sulfite-glycol chitosan or polyvinyl potassium sulfite-methyl glycol chitosan to obtain the objective semiconductor photocatalyst. The semiconductor photocatalyst is dispersed in water by 0.05 to 1 wt.% in a closed system and is irradiated with light such as sunlight, a mercury lamp, a xenon lamp, and a tungsten lamp, causing hydrogen and oxygen to be generated. The oxygen is removed by an absorbent or a liquid absorbent, allowing the hydrogen to be obtained.

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CLAIMS

[Claim(s)]

[Claim 1] The semi-conductor photocatalyst characterized by encapsulating a semi-conductor particle by the polymer.

[Claim 2] The semi-conductor photocatalyst characterized by encapsulating the particle of the titanium oxide which supported platinum, or a cadmium sulfide with the polymer of vinyl monomer polymer or polyvinyl potassium sulfate-glycol chitosan or polyvinyl potassium sulfate-methyl glycol chitosan.

[Claim 3] The semi-conductor photocatalyst characterized by using any one or more sorts of acrylic ester, methacrylic ester, styrene, or vinyl acetate as a vinyl monomer according to claim 2

[Claim 4] The manufacture approach of the hydrogen characterized by irradiating light at water under existence of a semi-conductor photocatalyst according to claim 1 to 3, and photodissociating water.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the approach of manufacturing hydrogen using the semi-conductor photocatalyst and this catalyst for photodissociating water etc. using light energies, such as the sun.

[0002]

[Description of the Prior Art] Many things which the same decomposition reaction occurs have been reported by by supporting platinum etc. also with a titanium oxide particle or other semi-conductor particles since [of generating of the hydrogen by disassembly of the water under the UV irradiation using the titanium oxide single crystal electrode and platinum electrode by Honda, Fujishima and others, and oxygen] a report (A. 44 Fujishima, KHonda;Bull.Chem.Soc.Jpn., 1148 (1971)). Sayama and others [especially] will have reported that the catabolic rate of water improves remarkably, if light is irradiated at the water solution which dissolved the carbonate under existence of the photocatalyst which consists of a zirconium dioxide which supported nickel oxide, ruthenium oxide, etc., or a tantalum oxide semi-conductor (KSayama, H.Arakawa;J.Photochem.and Photobio.A:Chem., 77,243 (1994)).

[0003] However, in order each of these approaches has the low generating effectiveness of hydrogen, and a photocatalyst carries out the optical dissolution by optical exposure and to prevent this dissolution When covering processing of the catalyst front face is carried out, a hydrogen generating function has the problem of being able to use only the light of an ultraviolet region which occupies that it cannot be discovered at all and about only 3% of solar energy, and the prospect of utilization of the hydrogen manufacture from the water by the sunlight using a semi-conductor particle has not left at all.

[0004]

[Problem(s) to be Solved by the Invention] It is offering the approach hydrogen's being manufactured cheaply and directly simple without passing through a solar battery etc. from the water and the sunlight using the purpose of this invention having the high generating effectiveness of hydrogen , and the optical dissolution of a catalyst not taking place at all , but being able to use [this invention can solve the above-mentioned technical problem , and] not only ultraviolet radiation but a visible ***** beam of light moreover , and offering the semi-conductor photocatalyst in which continuous duty's is possible , and this catalyst . . .

[0005]

[Means for Solving the Problem] this invention persons found out that the above-mentioned technical problem was solvable at once by encapsulating the so-called semi-conductor particle which is thin by the thickness of an Angstrom unit at an organic macromolecule, and covers one semi-conductor particle and one piece to homogeneity, as a result of advancing research wholeheartedly, in order to attain the above-mentioned purpose.

[0006] That is, this invention is a semi-conductor photocatalyst which consists of having ~~encapsulated the semi-conductor particle by the polymer~~ and encapsulates especially the particle of the ~~titanium oxide which supported platinum, or a cadmium sulfide~~ preferably with polymers, such as acrylic ester,

methacrylic ester, styrene, vinyl acetate, and polyvinyl potassium sulfate-glycol chitosan or polyvinyl potassium sulfate-methyl glycol chitosan.

[0007] Furthermore, it is the manufacture approach of the hydrogen which consists of irradiating light under existence of the above-mentioned semi-conductor photocatalyst at water, and photodissociating water as other this inventions.

[0008]

[Embodiment of the Invention] The energy difference of the upper limit of the valence band the electron of a semi-conductor is [valence band] full of the photoreaction using the semi-conductor of this invention, and the lower limit of the conduction band which is the orbit of the sky where an electron does not exist, Namely, if light with the energy more than a band gap (forbidden band) is irradiated, the electron of a valence band will be excited by the conduction band. An electronic defect, i.e., an electron hole, arises in a valence band, the electron of the generated conduction band passes an electron to a water molecule and other molecules, and returns [it moves to the interior of a semi-conductor easily and] to them, and the electron hole of a valence band uses the reaction which moves to an interface and oxidizes a water molecule and other molecules. If there is more than no electrolysis energy of the moisture solution whose potential difference of this band gap is 1.23V, water will not be disassembled into hydrogen and oxygen, and when the location of the lower limit of a conduction band is lower than energy-level H⁺ of hydrogen generating / H₂, hydrogen is not generated, and oxygen is not generated unless the upper limit of a valence band is lower than the location of energy-level O₂/H₂O of oxygen evolution.

[0009] Therefore, the potential difference of a band gap is more than 1.23V, and the semi-conductor which can be used for this invention has the location of the lower limit of a conduction band higher than energy-level H⁺ of hydrogen generating / H₂. As such ~~a semi-conductor particle~~, although SrTiO₃, TiO₂, CdTe, CdSe, Si, CdS, ZnS and Fe₂O₃, GaAs, GaP and InP, diamond powder, etc. can be mentioned, especially ~~amorphous or since TiO₂ or CdS of a rule mold can make~~ [many] the yield of hydrogen, it is desirable.

[0010] The one where particle size is smaller has the good generating effectiveness of hydrogen, and ~~this semi-conductor particle has that desirable 1 micrometer or less of whose particle size is 0.61 micrometers - 0.1 micrometers especially.~~

[0011] Although this semi-conductor particle can be used as it is, in order to generate hydrogen efficiently, it is 0.1 - 10% of the weight of the range about platinum, silver, copper, nickel oxide, ruthenium oxide, etc., and it is ~~desirable to support platinum 0.5 to 5% of the weight~~ and to use it especially. This support can use the known support approaches, such as the sinking-in method, settling, and an ion-exchange method.

[0012] ~~Although this invention encapsulates the above semi-conductor particles by the polymer~~ This encapsulation, stirring a semi-conductor particle and a monomer in a solvent. The polymerization method to which the polymerization of the monomer is carried out (see a macromolecule, 34, and 90 (1985)), The colloidal titration method using the principle of the colloid in which colloid with forward or negative charge has an opposite charge, and the colloidal titration which makes poorly soluble precipitate to a solvent in response to stoichiometric (see the Miyagi National College of Technology research bulletin, and 28 and 61 (1992)), Approaches, such as the compound coacervation method for using the electrostatic interaction of gelatin and gum arabic, can be used (see a microcapsule, Nikkan Kogyo Shimbun, and P68 (1970)).

[0013] As a monomer of the encapsulation in a polymerization method, a vinyl monomer is suitable and it is desirable to use acrylic ester, such as methacrylic ester, such as a methyl methacrylate, ethyl methacrylate, methacrylic-acid propyl, and methacrylic-acid butyl, a methyl acrylate, an ethyl acrylate, acrylic-acid propyl, and butyl acrylate, or styrene, vinyl acetate, etc. especially. In this polymerization method, specified quantity addition is carried out, a semi-conductor particle, water, and a monomer are carried out, and it keeps at room temperature -80 degree C, and a particle front face can be thinly microencapsulated by carrying out a polymerization, adding and stirring a polymerization initiator.

[0014] as the forward colloid in a colloidal titration method -- glycol chitosan (GCh) and methyl glycol

chitosan (MGCh) -- moreover, it is suitable to use polyvinyl potassium sulfate (PVS) as negative colloid. By this colloidal titration method, pH can be adjusted distributing the water solution of the above-mentioned forward colloid or negative colloid, and stirring said semi-conductor particle, a back titration can be carried out in the colloid water solution of an opposite charge, the point that condensation of colloid takes place rapidly can be made into the terminal point of colloidal titration, and a microcapsule can be thinly obtained for a particle front face by drying a ** exception.

[0015] Furthermore, about 50-degree C gelatin water solution is made to distribute said semi-conductor particle by the compound coacervation method. A gum arabic water solution is dropped at this, pH is adjusted to 3.5-4, and solution temperature is lowered to 5-8 degrees C. Formalin aqueous solution and alkali once adjusting pH to about 9 and making solution temperature into about 50 degrees C, in addition, by making it fall to a room temperature The microcapsule by which the particle front face was covered with gelatin gum arabic can be obtained.

[0016] In these capsulation, when making the amount of covering by the polymer into 2 or less % of the weight makes [many] the yield of hydrogen, it is desirable.

[0017] By making water distribute the semi-conductor photocatalyst encapsulated by the polymer obtained by the above-mentioned approach 0.05 to 1% of the weight by the sealing system, and irradiating light, such as sunlight, a mercury-vapor lamp, a xenon lamp, and a tungsten lamp, hydrogen and oxygen can occur, these gas can be taken out and hydrogen can be obtained by removing oxygen using the adsorbent or lean solution of oxygen. In addition, said water can be made to generate hydrogen for a sodium carbonate more efficiently with about 1 mmol concentration ***** in this case.

[0018] Since a hydrogen generating function does not fall even if it uses it repeatedly, the semi-conductor photocatalyst of this invention has the exposure section and the gas stripping section of light, and if the hydrogen manufacturing installation of the simple closed mold which consists of circulating the water which contains a semi-conductor photocatalyst for during this period is used, it can manufacture hydrogen cheaply and in large quantities from solar energy and water.

[0019]

[Effect of the Invention] The generating effectiveness of hydrogen is high, and the optical dissolution of a catalyst does not take place at all, but moreover this invention can use not only ultraviolet radiation but a visible ***** beam of light, and does so the effectiveness according to rank that continuous duty is possible, and hydrogen can be manufactured cheaply and directly simple without passing through a solar battery etc. from water and sunlight.

[0020]

[Example]

In the adjustment rutile type titanium dioxide of a photocatalyst, an anatase mold and amorphous mold titanium oxide, and a list, it added 1% of the weight, and for 30 minutes, it ground, platinum black was kneaded [the cadmium sulfide was taken to the agate mortar respectively,], and the photocatalyst of platinum support was prepared. As a result of measuring these particles with a scanning electron microscope (SEM) photograph, the mean diameter of a rutile mold and anatase mold titanium oxide was [about 0.02 micrometers and ~~the cadmium sulfide of about 0.02 micrometers~~ and amorphous mold titanium oxide] about 0.1 micrometers.

[0021] Capsulation 1 The titanium oxide of the rutile mold which supported the platinum of the polymerization method above, an anatase mold, or an amorphous mold, monomer 0.7g which 300ml of water was distributed, maintained 13g at the temperature of 65 degrees C, and was shown in Table 1, and 5x10 to 3 mol/l. polymerization initiator concentration are applied, it stirred for 3 hours and the polymerization was carried out, respectively. Moreover, the polymerization was performed to the rutile type titanium dioxide of platinum support like the above using 10g [of mixture], and monomer 0.5g which mixed the amorphous mold titanium oxide of platinum support 3% of the weight. The ** exception, it washed and dried and these capsulation objects measured conversion and polymer content. This result was shown in Table 1.

[0022] As a result of observing these capsulation objects with a scanning electron microscope (SEM) photograph, all of the covering condition of a particle and the distributed condition were good.

[0023]

[Table 1]

実験 No.	TiO ₂ 結晶型	モノマー	重合開始剤	重合率 (%)	ポリマー含有量 (wt%)
1	ルチル	メタクリル酸メチル	AIBA	3.6	0.2
2	アナ-ゼ	ステレン	AIBN	4.5	0.3
3	アモルファス	メタクリル酸メチル	亜硫酸	1.8	0.1
4	アモルファス	アクリル酸アクリル	亜硫酸	6.3	0.3
5	TiO ₂ 混合物	メタクリル酸メチル	亜硫酸	18.3	1.0

(AIBA : 2,2'-アゾ-2'スイリグチオアミン塩酸塩、AIBN : アゾビススイリグチオニトリル)

[0024] 2) 15ml of 1 [1.0g and]/N [400] PVSK water solutions was made to distribute the mixture and the cadmium sulfide which added platinum support amorphous mold titanium oxide 3% of the weight to the rutile type titanium dioxide of platinum support of the colloidal titration method above, and the rutile type titanium dioxide of platinum support, respectively, the acetic acid was added, and pH was adjusted to 4.0 and stirred for 1 hour or more. Then, by 1/N [200] GCh, to the point which condensation of colloid produces rapidly, the back titration was carried out and it dried the ** exception. The measurement result of the polymer content of these encapsulation objects was shown in Table 2.

[0025] Moreover, as a result of observing these with a scanning electron microscope (SEM) photograph, the covering condition of a particle and the distributed condition were good.

[0026]

[Table 2]

実験 No.	半導体粒子の 種類	ポリマー含有量 (wt%)
6	Mn/TiO ₂	0.5
7	TiO ₂ 混合物	1.0
8	CdS	1.1

[0027] Added 0.2g of encapsulated semi-conductor photocatalysts which were obtained by the hydrogen generating evaluation test above to 300ml of sodium-carbonate water solutions of 0.28 mol/l in a quartz flask, they were made to suspend with a magnetic stirrer, and the optical exposure was carried out using 500W xenon lamp (USHIO, INC. UXL-500D). With time, generating hydrogen (ml) was measured with micro view let and gas chromatography (column: molecular-sieve 5A, a carrier gas:argon, detector:TDC, 60 degrees C).

[0028] Moreover, hydrogen was generated by the same approach also about the semi-conductor particle which did not perform encapsulation by the polymer with a platinum support rutile type titanium dioxide (experiment No.9), this anatase mold titanium oxide (experiment No.10), amorphous mold titanium oxide (experiment No.11), and this cadmium sulfide (experiment No.12) for the comparison.

[0029] These results were shown in Table 3. In addition, the hydrogen yield in Table 3 is ml, and it is the amount of accumulation, and experiment No. is the same as the thing of encapsulation.

[0030]

[Table 3]

実験 No.	60 分	120 分	180 分	240 分	300 分
1	1.3	3.0	4.0	5.3	6.2
2	1.2	2.8	3.7	5.0	6.0
3	3.8	6.2	8.3	9.2	9.7
4	4.7	7.2	9.3	11.2	13.0
5	0.8	2.2	3.3	3.8	4.2
6	4.3	7.0	8.8	10.5	11.5
7	0.8	2.2	3.3	3.8	4.2
8	5.8	8.7	10.8	12.8	14.3
9	0.4	1.2	1.5	2.0	2.0
10	0.5	1.3	2.0	2.5	2.5
11	3.7	5.7	7.2	8.0	8.5
12	0	0	0	0	0

[0031] These results show that the encapsulated semi-conductor photocatalyst can generate much hydrogen compared with what is not being encapsulated (No.1, 5 and 6, 7:No.9, No.2:No.10, No.3, 4:No.11, No.8:No.12).

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